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(54) Deposition of diffusion carbide coatings on iron-carbon alloy articles

(57) The articles are heated while immersed in a powder mixture containing a carbide-forming element, a carbon-containing compound, an activator, and an inert filler, to a temperature of 560 to 720°C, at which temperature the surface of the articles is carburized over a period of 0.6 to 1.2 h. Then the carburized article is heated to a diffusion-saturation temperature of 950 to 1100°C at a rate of 0.8 to 2.4 °C/s. at which temperature the surface of the article is diffusion-saturated with the carbide-forming element at a temperature over a period of time of 1.2 to 1.8 h. Upon expiration of the diffusion saturation time the article is cooled at 1.2 to 2.4 °C/s to a temperature of 300 to 500°C. Then all the above-listed operations are repeated at least once. The carbide-forming element may be Cr, Mo, W, Nb, Zr, Ta, Si. The carbon-containing compound may be diphenyl, naphthalene, anthracene, pyrene, triphenylene, 3,4-benzo-pyrene or polyvinyl chloride (Ex 3); the activator may be ammonium chloride, ammonium fluoride, ammonium iodide or ammonium bromide; and the filler may be aluminium oxide, magnesium oxide or silicon.

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DEPOSITION OF DIFFUSION CARBIDE COATINGS ON
IRON-CARBON ALLOY ARTICLES

5 The present invention relates to metallurgy, is concerned with thermochemical treatment of metals and alloys and, more particularly, with methods of depositing diffusion carbide coatings on iron-carbon alloy articles.

10 To extend durability and service life of the parts of machines and mechanisms subjected to heavy wear, they are diffusion saturated, thus producing a diffusion coating on their surface. This coating should feature a higher hardness and wear resistance than those of the material of the article. These requirements are met most fully by the carbide-type diffusion coatings.

15 One of the commonest methods for depositing metal carbide coatings on various articles, including those made from iron-carbon alloys, is the method of chemical deposition of carbides from the vapour phase (Chemical Vapour Deposition).

20 The equipment for depositing carbide and other types of coatings produced on a mass scale by "Plansee" (Austria), "Berna AG" (Switzerland), "Konsarc" (USA), Scientific Coatings Inc. (USA), Troy (USA), PED Ltd (Great Britain), Coleshill (Great Britain), "Sandvic"
25 (Sweden), etc. ensures a highly efficient process by introducing multiple-module installations and increasing the active volume of reaction vessels. Thus, depositing a chromium carbide coating of a stoichiometric composition Cr_{23}C_6 or Cr_7C_3 or a mixture of
30 these carbides on steel tools permits using the latter at _____

temperatures up to 950°C inclusive and extends their service life 20-25 times. The carbide layer is produced on the heated surface of the article due to chemical interaction of chromium haloid with methane. The articles are
5 placed into a reaction vessel, vacuumized, heated and, as the temperature rises to 850-1050°C, the gaseous mixture of chromium haloid, methane (CH_4) and carrier gas is introduced into the reaction vessel.

The carbide layer up to 12 μm thick ensures a high
10 wear resistance. The thickness of the carbide layer exceeding 12 μm which in some cases is required for better operational and tribological properties of articles results in decarburization of the sublayer zone, i.e. the layer of base material lying directly under the carbide layer,
15 which affects adversely said properties. Besides, in such a process of depositing carbide coatings the rate of growth of the carbide layer does not, as a rule, exceed 2 $\mu\text{m/h}$ which increases its duration.

The coatings of chromium carbide Cr_7C_3 are deposited
20 at a considerably higher rate and at lower temperatures by decomposition on the heated surface of the workpiece of the vapours of bis-ethyl benzene in vacuo. To prevent formation of dendrites in the coating, the process is conducted under non-isothermal conditions: at the first
25 stage at 300-350°C in the course of 10 min followed by 50 minutes at 500-600°C. The pressure in the working chamber is 1.33 Pa. The thickness of the chromium carbide

layer deposited in this way is $340\text{ }\mu\text{m}$; the layer features a high wear resistance and a microhardness of 2500 NV. However, such coatings are unsuitable under high specific loads, especially under alternating loads and considerable tangential stresses since this causes peeling of the carbide layer due to a low adhesion strength on the boundary with the base metal.

Chromium carbide coatings deposited at higher temperatures are noted for a considerably higher strength of adhesion to the base metal. One of the prior art methods comprises a preliminary treatment of the workpiece surfaces with a solution containing 5-20% HNO_3 and 10% fluorides followed by coating them with a suspension based on chromium powder. The suspension is prepared from a solution of organic binder, for example acrylic resin in a solvent, e.g. methyl chloroform. Now the diffusion coating is deposited by immersing the workpieces into a retort filled with a mixture of powders through which argon or hydrogen is passed at $900\text{-}950^\circ\text{C}$ in the course of 2- 10 h. However, this technology is little productive, requires much labour while the use of volatile organic compounds calls for extra and enviromental protection (US Patent No. 4347267, IPC B05D 7/22, B05D 7/14, NPC 427/237, publ. 31.08.82).

The amount of labour required for depositing diffusion chromium carbide coatings can be curtailed considerably by heating the surface with HF currents. The saturating mixture containing chromium and halogen-containing compounds is freely strewn over the treated surface. The

equipment used in the process includes a water-cooled inductor and, if necessary, a separator made of a nonmetallic material. This method is economical due to localization of the heated surfaces and a possibility of reclaiming the material utilized in deposition of coatings. At the same time, it should be pointed out that the carbide coatings deposited in this way are nonuniform with respect to thickness, chemical and phase composition because heating of workpieces with HF current fails to provide for uniform distribution of temperature on the treated surface (Laid-open application of Great Britain No. 2109822 it, IPC C23C 9/02, publ. 08.06.83).

It is noteworthy that all the above-described methods lead to decarburization of the sublayer zone which cuts down the permissible contact pressure on the strengthened surface during subsequent operation of the coated article. This is attributed to diffusion of carbon contained in iron-carbon alloys into the layer of the deposited carbide-forming element resulting in the formation of carbides.

With a view to reduce or eliminate altogether the effect of decarburization of the sublayer zone, a general practice is to saturate the surface in two stages: preliminary saturation of the surface layer with carbon or nitrogen followed by deposition of the carbide-forming element. The carbon or nitrogen introduced into the surface layer at the first stage forms carbides, nitrides or carbonitrides at the second stage, thus preventing the decarburization of the sublayer zone.

Patented in the USA is a method for depositing diffusion coatings based on chromium carbide on the surface of steel articles containing at least 0.2% of carbon. The preliminary fine nitriding is conducted to a depth of 100-350 μm in the atmosphere of a nitrogen-hydrogen mixture at 450-650°C in the course of 5 - 40 h to produce 1.5 - 2.5% of nitrogen in the nitrided layer. At the second stage of the process consisting in gas chromizing in the course of 5 - 30 h at 850 - 1100°C, the formed layer of chromium carbide is up to 40 μm thick and features a high resistance to wear. It should be noted that the process for the deposition of such coatings is very long, calls for considerable expenditures of electric power and cannot be regarded as a highly efficient process (US Patent No. 4242151, IPC C23C 11/04, 11/16, publ. 30.12.80).

Known in the prior art is chromizing in a reducing atmosphere based on hydrogen in a pulverized mixture of ferrochromium, 0.4-1.0% of ammonium chloride and chromium (50-75%). While treating steel articles containing more than 0.35% carbon, 0.5 - 1.5% of ammonium fluoride is added to the chromium-plating mixture. The necessity for using the hydrogen atmosphere in the course of heating cuts down the economy of such a process and calls for the provision of special fire and explosion preventive measures. (French application 1/18 No. 2439824, Cl. C23F 17/00, publ. 23.05.80; French Patent No. 2483468, Cl. C23C 9/00, publ. 4.12.81).

Similar results are achieved by practising at the first stage liquid nitriding in the medium of molten nitrate

in the course of 12-150 h which reduces sharply the efficiency of the process (French application No. 2454471, Cl. C23C 11/04, 11/14, publ. 14.11.80).

5 It is also possible at the first stage of the process to use carburizing, boronizing or sulphurizing; the chromium carbide coatings produced in this manner possess a high resistance to wear.

10 In some cases the process of nitriding or carburizing in a liquid or gaseous medium is conducted after depositing a layer of carbide-or nitride-forming element on the treated surface. The carbide, nitride or carbonitride layer is also characterized by a high wear resistance though the adhesion strength of such a coating is substantially lower than that of the previously described coatings (GDR Patent
15 No.2005730, IPC C23F 17/00, publ. 18.05.83).

However, the two-stage treatment consisting of such successive operations as saturation of the surface layer of the work with carbon, nitrogen or boron and deposition of a carbide or nitride-forming element, in any sequence,
20 calls for a very long duration which worsens the economical and technical parameters of the process as a whole.

The speedy formation of the carbide layer of steel articles can be achieved also by diffusion saturation in an antimony melt with introduced particles of alloying,
25 including carbide-forming, elements, e.g. chromium. The work is immersed into the melt, heated to 1090°C and held so for 5 h; this is accompanied by migration of atoms of alloying elements to the surface of the work

with subsequent diffusion into the material of the article (Gene Wolfe Breakthrough in diffusion alloying. "Plant Engineering" (USA), 1976, 30, No. 25, p. 127-128). Still, such a technological process cannot be regarded as universal and promising from the ecological viewpoint.

The methods for production of diffusion carbide coatings developed in Japan, named "Toyota-Diffusion" combine a sufficiently high capacity with adaptability to production. The workpiece is placed into a crucible filled with a melt of anhydrous borax ($\text{Na}_2\text{B}_4\text{O}_7$), boric oxide (B_2O_3) or compound $\text{K}_2\text{B}_4\text{O}_7$. Depending on the required composition of the carbide coating, the borax melt is mixed with alloying carbide-forming elements in the form of their pulverized compounds in the amount of 1 - 60%. The content of the carbide-forming compound should be not less than 30% of the borax content. The function of the carbide-forming elements may be fulfilled by chromium and metals of Va group of Mendeleeff's periodic law vanadium, niobium and tantalum. The compound of these elements may take the form of a ferro-alloy or oxide (US Patent No. 4158578, IPC C23C 9/10, publ. 19.06.79) at a mass relation of boron and oxide within 7 - 40%, oxide and chromium as a pure metal or alloy thereof (US Patent of No. 4230751, IPC C23C 9/16, C25D 3/66, publ. 28.10.80., US Patent No. 4202705, IPC C23C 9/10, publ. 13.05.80).. The process is conducted at $850-1100^\circ\text{C}$ within 1 - 20 h. The coatings produced in this manner have a high resistance to wear but this method presupposes subsequent dressing of the work surface; besides, the surface

of such articles after deposition of coatings is inevitably oxidized and requires in a number of cases additional machining to impart the necessary surface roughness to the article.

5 What is desired is a method of depositing diffusion carbide coatings on iron-carbon alloy articles which would improve the physicomechanical properties of the coating and, particularly, hardness and wear resistance, thereby extending the service life of the articles.

10 The present invention provides a method of depositing a diffusion carbide coating on one or more iron-carbon alloy articles comprising:

- loading a container with a powder mixture comprising solid components: at least one
15 carbide-forming element, at least one carbon-containing compound, activator, inert filler, and immersing the article(s) into said mixture;
- heating said article(s) to a surface carburization temperature selected from 560 to 720°C;
- 20 - carburization of the surface of the article(s) at a temperature from 560°C to 720°C within a period of time from 0.6 h to 1.2 h;
- heating the carburized article(s) to a temperature of diffusion saturation of the surface with a
25 carbide-forming element, said temperature ranging from 950 to 1100°C at the rate from 0.8°C/s to 2.4°C/s;
- diffusion saturation of the surface of the article(s) with a carbide-forming element or elements at a temperature from 950°C to 1100°C within a period of
30 time from 1.2 h to 1.8 h;
- cooling the article(s) with the deposited carbide coating at the rate from 1.2°C/s to 2.4°C/s to a temperature from 300 to 500°C;

- repeating at least once the above-listed operations beginning from heating the article(s) to a carburization temperature.

5 For depositing diffusion carbide coatings imparting the highest surface hardness and wear resistance to the articles, the above-listed operations should preferably be repeated up to seven times.

10 The herein-disclosed method allows the physicomachanical properties of coatings, such as wear resistance, to be raised 2.8 - 3.3 times compared with the known method. As a consequence, the service life of the articles protected by such coatings is extended 2.5 - 3.0 times, compared with the known coating.

15 Given below is a detailed description of the preferred method of depositing diffusion carbide coatings on iron-carbon alloy articles.

20 Deposition of diffusion carbide coatings on iron-carbon alloy articles is based on contact deposition from the gaseous phase in the powder mixture comprising carburization of the article surface followed by diffusion saturation with carbide-forming elements. The powder mixture contains the following solid components: carbide-forming element, carbon-containing compound, _____

activator and inert filler. The carbide-forming element may be constituted by chromium, molybdenum, tungsten, niobium, zirconium, tantalum, silicon; or a mixture thereof. The carbon-containing compound may be diphenyl, naphthalene, anthracene, pyrene, triphenylene, 3,4-benzo-pyrene. In addition to the above-named organic compounds another solid organic compound of the hydrocarbon class may be used; this organic compound should be in a solid state at room temperature, its boiling or sublimation temperature ranging from 100 to 700°C. The function of activator may be fulfilled by ammonium chloride, ammonium fluoride, ammonium iodide, ammonium bromide. Aluminium oxide, magnesium oxide, or silicon dioxide may be used for inert filler.

The powder mixture is prepared by sifting all the components taken separately in the form of powders through a vibrosieve with a mesh not over 50 μ m. The particle size of the sieved fraction should not exceed 50 μ m. The particles of this size ensure a high saturation rate of the surface with carbon at the carburization stage and with carbide-forming element at the diffusion saturation stage. Besides, the use of the powder mixture with particles of this size precludes sticking of the mixture particles to the surface of the work. After sifting, each component is weighed out in the following proportions mass %:

| | |
|----------------------------|-------------|
| carbide-forming element | 40 - 70 |
| carbon-containing compound | 0.5 - 2.5 |
| activator | 0.2 - 5.0 |
| inert filler | the balance |

After weighing, each component of the powder mixture is dried under certain conditions, depending on the nature of the component. The powder of the carbide-forming element is dried at 140°C in the course of four hours. The powder of inert filler is calcinated at 1200°C for two hours. The carbon-containing compound is dried at 60°C within 0.5 - 1.0 h. And the activator powder is dried at 140°C during four hours. Then all the components are cooled down to 40°C and thoroughly mixed in a biconic mixer for 1 - 2 h.

The moisture content in the powder mixture intended for use in the process of preparation of diffusion carbide coatings shall not exceed 5 - 6%. Said powder mixture is placed into a stainless steel container. The articles are immersed into the mixture so as to leave a distance of at least 20 mm from the container bottom to the article, 10 mm from the container side walls to the container, at least 51 mm between the articles, and at least 30 mm from the articles to the first container cover.

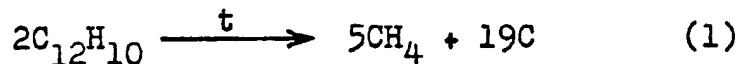
After the articles have been immersed into the powder mixture, the container is closed by the first cover of stainless steel, and a layer of quartz sand at least 30 mm thick is poured on top of it. Then the second cover is closed and boric oxide B_2O_3 , a substance with a melting temperature of about 450°C is poured on top of it.

The container with the powder mixture and articles is placed into a resistor furnace and heated to a temperature from 560 to 720°C ; then the surface of the articles is

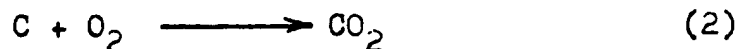
carburized; said carburization, according to the invention, is conducted at a temperature of 560 to 720°C

for from 0.6 to 1.2 h. The mechanism of chemical reactions occurring inside the container in the course of the process can be explained by way of example of a powder saturating mixture consisting of chromium, diphenyl, ammonium fluoride, and aluminium oxide. The aluminium oxide is an inert filler and takes no part in the chemical reactions.

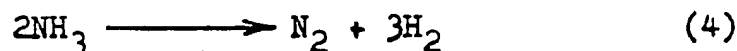
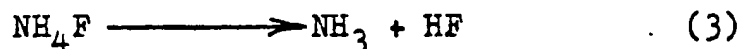
10 In the course of heating, beginning from a temperature of approximately 256°C, diphenyl is decomposed:



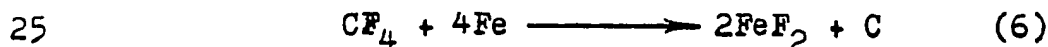
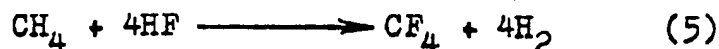
Carbon interacts with the oxygen inside the container:



15 Beginning from a temperature of 335°C the ammonium fluoride is decomposed:



Then saturated hydrocarbon (methane) formed during decomposition of diphenyl interacts with a part of hydrogen fluoride, thus forming carbon tetrafluoride which is adsorbed by the surface of the article, forming active atoms of carbon which saturate the surface of the article:

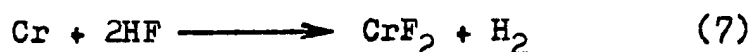


Reactions (5) and (6) take place, mainly, within the time of carburization.

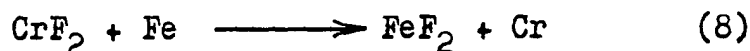
As the temperature in the furnace reaches 450°C, boric

oxide B_2O_3 melts, forming a compact layer which seals off the container and prevents the air along with the oxygen it contains from penetrating into the container.

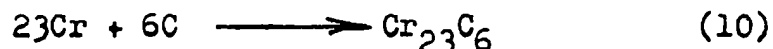
As the temperature rises to $814^{\circ}C$, chromium in the container starts evaporating, interacting with hydrogen fluoride and creating an active gaseous medium for diffusion saturation.



Chromium fluorides are adsorbed by the surface of the article, forming active atoms of chromium which diffuse into the surface layer of the article:



Interacting with the carbon that has diffused into the surface of the article at the carburization stage, the active atoms of chromium form a diffusion carbide coating:



Reactions (7) - (10) proceed most intensively at a temperature selected from a range of 950 to $1100^{\circ}C$.

Carburization allows the surface layer of the article to be saturated with carbon which diffuses into the article from the powder mixture thus ensuring during subsequent heating the accelerated formation of the diffusion carbide layer. The diffusion carbide layer is formed only by the carbon that the diffused into the surface of the article from the powder mixture. The carbon contained in the material of the article does not diffuse into the surface of the

article for creating the carbide layer. This practically rules out the formation of a decarburized zone under the coating which is present in the other prior art methods. At the carburization stage the carbon-containing compound
5 is decomposed and evolves a large amount of gaseous saturated hydrocarbons and a certain amount of carbon dioxide in interaction with the oxygen in the air and with steam which are present in small amounts in the container in accordance with reactions (1) and (2). Interaction of the
10 products of decomposition of the carbon-containing component with hydrogen halide formed during decomposition of the activator results in the formation of a gaseous compound of carbon with one of halogens, e.g. carbon tetrafluoride according to reaction (3) which intensifies saturation of
15 the surfaces with carbon. Holding the articles at these temperatures provides for saturation of the surface layer with carbon which ensures fast formation of the carbide layer during subsequent heating. The desired effect will not be achieved if the above-stated temperature and time
20 limits are not adhered to. Carburization at temperatures below 560°C fails to ensure sufficient diffusion flow of carbon from the products of decomposition of the carbon-containing compound of the mixture into the surface layer of the article. Carburization at a temperature above
25 720°C results in premature precipitation of the carbide-forming element on the surface of the article and its subsequent diffusion. If the carburization time is under 0.6 h,

concentration of carbon on the surface of the article diminishes causing formation of a decarburized zone under the diffusion coating. The decarburized zone reduces the strength and tribological characteristics of the article with a
5 diffusion carbide coating. If the carburization stage takes longer than 1.2 h, this is inexpedient from the economical point of view because the strength and tribological characteristics do not grow any more while there is an unwarranted expenditure of power.

10 On expiration of the carburization time the articles are heated to the diffusion saturation temperature, the heating being conducted at a rate selected from 0.8 to 2.4°C/s. This procedure ensures a constant concentration of carbon above the surface layer of the article saturated with
15 carbon that has diffused into said article from the powder mixture at the carburization stage and prevents formation of the decarburized zone under the diffusion carbide coating at the stage of diffusion saturation. Heating to the diffusion saturation temperature at the rate higher
20 than 2.4°C/s is impracticable from the viewpoint of economy since it involves a large amount of energy spent by more powerful heaters. Conversely, heating conducted at the rate lower than 0.8°C/s results in diffusion dispersal of carbon from the surface layer; said carbon begins diffu-
25 sing into the article, i.e. into the matrix thereby reducing the concentration of carbon in the surface layer. At the diffusion saturation stage this results in that the amount of carbon diffused into the surface layer at

the carburization stage proves insufficient for forming the diffusion carbide layer; as a consequence, the carbon starts diffusing from steel thereby creating a decarburized zone under the carbide layer.

5 On reaching the temperature lying within the diffusion saturation temperature bracket from 950 to 1100°C, heating is discontinued and diffusion saturation is conducted within a time period selected from 1.2 to 1.8 h. This procedure creates a diffusion carbide layer on the
10 surface of the article. The formation of the diffusion carbide layer is ensured by the interaction of the carbide-forming element deposited on the surface, with carbon that has saturated the surface layer of the article according to (1). Within these time periods the carbon included
15 into the material of the article takes practically no part in the formation of the diffusion carbide layer which rules out the formation of a decarburized zone under the diffusion carbide layer. It should be noted that, inasmuch as the surface layer of the article is saturated with
20 carbon, the carbide layer is formed more vigorously than it is in the methods known heretofore. The desired effect will not be gained if the above temperature and time intervals are not complied with. Diffusion saturation conducted at temperatures below 950°C results in a reduction
25 of thickness of the diffusion carbide layer through insufficient diffusion of the carbide-forming element into the coating which impairs the strength and tribological characteristics of the coating. Diffusion saturation

conducted at temperatures higher than 1100°C is equally
inexpedient since at such temperatures the grains of the
article material increase in size thereby impairing the
mechanical properties of the article, viz., its impact
5 strength. If diffusion saturation is conducted within
less than 1.2 h, this results in an insufficient deposi-
tion rate of the carbide-forming element on the surface of
the article and in the formation of a thinner diffusion sa-
turation layer thereby impairing the strength and tribo-
10 logical characteristics of the coating. Conversely, extend-
ing the time of diffusion saturation beyond 1.8 h results
in the formation of a diffusion carbide layer with a lower
concentration of carbon since under these conditions the
carbon will diffuse through already formed carbide layer,
15 the diffusion process will lose its intensity so that
concentration of carbon in the surface layer will diminish.
Apart from that, at such diffusion saturation time it may
happen that carbon will diffuse from the matrix into the
coating since the entire amount of carbon introduced into
20 the surface at the carburization stage will already have
been used up for creating the carbide layer while diffu-
sion of the carbide-forming element will continue. This
effect brings about the formation of a decarburized zone
under the coating.

25 On expiration of diffusion saturation time, the con-
tainer with articles is cooled at the rate, according to
the invention, selected with the limits from 1.2 to 2.4°C/s
to a temperature selected from 300 to 500°C .

This technique makes it possible to avoid the effect of carbon redistribution under the diffusion carbide layer and formation of a decarburized zone under the coating. At these cooling rates the carbide-forming element and carbon stop settling on the surface of the article from the powder mixture so that there is no diffusion of carbon from the matrix to the surface of the article. Cooling after diffusion saturation at the rate higher than 2.4°C/s is impractical economically since it calls for the use of a special cooling system. Conversely, cooling the container after diffusion saturation at the rate below 1.2°C/s will result in deposition of the carbide-forming element on the surface causing diffusion redistribution of carbon in the carbide layer which will diffuse to the surface for forming carbide but at a lower rate, and producing a decarburized zone under the carbide coating, which is strongly objectionable.

After cooling to a temperature selected from the interval of 300 to 500°C the entire process of treatment explained above is repeated, according to the invention, at least once, the number of cycles reaching seven. The number of cycles with these limits should be selected to suit the service conditions of the articles with diffusion coating. If the cycles are repeated 6 or 7 times, produced coating features high strength and tribological characteristics.

On cyclization of the above-described process of treatment with carburization within $560 - 720^{\circ}\text{C}$ the diffu-

sion carbide layer created in the preceding cycle is saturated with carbon from the powder mixture and, in the course of further heating, diffuses into the layer of deposited carbide-forming element followed by the formation of its carbides. Cyclization speeds up the growth of the diffusion carbide layer without reducing the concentration of carbon in the sublayer zone. In addition, the cyclic nature of the temperature conditions of saturation with periodical cooling to a temperature selected from the interval of 300 to 500°C forms a diffusion carbide layer of a more dispersed structure. This is due to the fact that repeating the cycle of two-stage heating after cooling to a temperature from 300 to 500°C results not in the growth of the already existing carbide crystals, but in the formation of new nuclei of crystallization of the carbide-forming element and development of carbides on the surface being treated. This produces a multiplicity of fine carbide crystals which improves the strength and tribological characteristics of the article. The completion of the cooling process at temperatures higher than 500°C denies the possibility of formation of new crystallization nuclei so that further heating and carburization brings about only the growth of the existing carbide crystals without creation of the finely-dispersed structure. The completion of cooling at temperatures below 300°C is inexpedient from the economical standpoint as this involves an extra amount of electric power for subsequent heating. If the number of cycles is less than two, the meaning of the notion

"cyclic process" is lost. At a number of cycles exceeding eight, the powder mixture becomes depleted, i.e. the amount of carbon diffusing from the mixture into the surface of the article diminishes which, in turn, results in a longer holding time during each cycle and, on the whole, in an unwarranted prolongation of the process and an additional expenditure of power.

On completion of the required number of cycles, heating is discontinued and the container is cooled in the air to room ambient temperature. Then the container is opened for removing the articles and the powder mixture. The articles are sent to the Customer while the powder saturating mixture is turned over for reclaiming. Reclaiming consists in grinding the powder mixture in a ball mill, sifting it through a vibrosieve, mesh $50\text{ }\mu\text{m}$, drying at 140°C for 4 h and adding the dried activator and carbon-containing compound in the following proportions, mass %: 0.5 - 2.5 of carbon-containing compound, 0.2 - 5.0 of activator. The used mixture is carefully mixed with activator and carbon-containing substance. Then freshly-prepared and dried powder mixture is added at the rate of 10% of the initial weight of the mixture, and carefully mixed again. Now the powder mixture can be used as required. The mixture can be reclaimed up to 15 times before discarding it.

The herein-proposed method produces compact non-porous diffusion carbide coating $21.0 - 40.0\text{ }\mu\text{m}$ thick, with a microhardness of 21.5 - 27.0 GPa, average height of carbide crystals $4.2 - 5.4\text{ }\mu\text{m}$, hardness of base ma-

terial 4.2 - 7.4 GPa, minimum hardness in sublayer zone 4.2 - 7.4 GPa, absence of decarburized zone under the carbide coating and a relative wear rate in sliding friction of 12.5 - 16.5 g/m².s.

5 The carbide coating is of an attractive silvery-grey colour, surface roughness Ra being not over 0.32 um; on completion of the process, the article does not require any dressing and subsequent machining. The coating is spread uniformly over the entire surface of the
10 article including the interval spaces and adheres efficiently to the material of the article.

 The process does not call for the use of vacuum apparatuses, nor does it use gases (hydrogen and argon) which necessitate the provision of special fire and explosion prevention facilities. The process does not entail
15 any substantial danger to the attending personnel and environment.

 Though the process may be repeated up to 7 times, its total duration does not exceed 20 - 22 h because of
20 a short duration of its individual stages.

 The present invention will be made more apparent by way of example of embodiment of the method for depositing diffusion carbide coatings on iron-carbon alloy articles.

Example 1

25 A stainless steel container of 80 mm inside diameter, 110 mm high, wall thickness 5 mm, is charged with 300 g of a powder mixture containing 195 g chromium powder (65%), 3 g diphenyl C₁₂H₁₀ (1%), 1.5 g ammonium chloride NH₄Cl(0.5%)

and 100.5 g aluminium oxide Al_2O_3 (33.5%).

These components are ground in advance, sifted to produce a fraction of a grain size under $50\text{ }\mu\text{m}$, weighed out according to the formula and mixed in a mixer.

5 Then specimens of carbon and alloy steels 15 mm
in diameter, 5 mm high, are immersed into said mixture
leaving a distance of 20 mm between the container bot-
tom and the specimens, 10 mm between the container side
walls and the specimens, 15 mm between the specimens,
10 and 30 mm between the specimens and the first cover of
the container. The specimens are arranged in one row.
Having placed the specimens in the powder mixture, the
container is closed with the first stainless steel cover,
pouring a layer 30 mm thick of quartz sand on top of
15 said cover. Then the second stainless steel cover of the
container is closed, a layer of boric oxide 10 mm thick
is poured on top of said cover and the container is
moved into a resistor furnace. The container is heated
to 650°C and carburization is conducted for 1.0 h at this
20 temperature. The surface of the specimens is saturated
with carbon. The carburized specimens are then heated to
a diffusion saturation temperature (1000°C) at the rate
of 1.5°C/s . As soon as the temperature of 1000°C has been
reached, it is maintained for 1.5 h for diffusion satura-
25 tion of the specimen surface with chromium. On completion
of diffusion saturation with chromium the specimens are
cooled to 400°C at the rate of 1.8°C/s . Then the above-listed

operations of heating to the carburization temperature, carburization proper, heating to the point of diffusion saturation, diffusion saturation and cooling are repeated once more followed by cooling the container with the specimens in the air to the ambient temperature. Now the container is opened, the powder saturating mixture is turned over for reclaiming while the specimens are tested by conventional methods to determine the physicomachanical and physicochemical properties of the produced carbide-chromium coating.

Test results:

- carbide coating is compact, i.e. practically without pores;
- thickness of carbide coating, $21.0\mu\text{m}$;
- microhardness of carbide coating, 21.6 GPa;
- average height of carbide crystals, $5.2\mu\text{m}$;
- hardness of base material, 5.6 GPa;
- minimum hardness of sublayer zone, 5.6 GPa;
- relative wear rate $12.5\text{ g/m}^2\cdot\text{s}$.

Example 2

The diffusion carbide coatings are prepared in a container described in Example 1. The container is charged with 300 g of a mixture containing 195 g of titanium powder (65%), 3 g of anthracene $\text{C}_{14}\text{H}_{10}$, (1%), 1.5 g of ammonium bromide NH_4Br (0.5%), and 100.5 g of magnesium oxide (33.5%). The powder mixture is prepared as in Example 1. The specimens are used and arranged in the container as in Example 1. The container with the powder

mixture and specimens is placed into a resistor furnace and heated to 560°C . At this temperature the specimens are carburized during 1.2 h with resultant carburization of their surface. The carburized specimens are heated to 950°C at the rate of 2.4°C/s . This is the temperature at which the surface of the articles is diffusion-saturated with titanium. The diffusion saturation lasts for 1.8 h. On completion of diffusion saturation with titanium the specimens are cooled down to 500°C at the rate of 1.2°C/s . Then the above operations of heating to the carburization temperature, carburization proper, heating to the stage of diffusion saturation, diffusion saturation proper and cooling are repeated three times more. Now the container is opened, the saturating powder mixture is turned over for reclaiming and the specimens are tested by conventional methods for determining the physicommechanical and physicochemical properties of the deposited titanium-carbide coating.

Test results:

- carbide coating is compact, i.e. practically without pores;
- thickness of carbide coating, $28.8\text{ }\mu\text{m}$;
- microhardness of carbide coating, 26.8 GPa;
- average height of carbide crystals, $4.7\text{ }\mu\text{m}$;
- hardness of base material, 4.2 GPa;
- minimum hardness in sublayer zone 4.2 GPa;
- relative wear rate, $18.2\text{ g/m}^2\cdot\text{s}$.

Example 3

The diffusion carbide coatings are prepared in a container described in Example 1. The container is charged with 300 g of a powder mixture containing 195 g of silicon powder (65%), 3 g of naphthalene $C_{10}H_8$ (1%), 1.5 g of ammonium iodide NH_4I (0.5%) and 100.5 g of aluminium oxide Al_2O_3 (33.5%). The powder mixture is prepared as in Example 1. The specimens are used and arranged in the container just as in Example 1. Then the container with the powder mixture and specimens immersed therein are placed into a resistor furnace and heated to $720^{\circ}C$. At this temperature the specimens are carburized for 0.6 h so that their surface becomes carburized. Then the carburized specimens are heated to $1100^{\circ}C$ at the rate of $0.8^{\circ}C/s$. This is the temperature of diffusion saturation of the surface of specimens with silicon. The diffusion saturation is conducted for 1.2 h. On completion of diffusion saturation with silicon the specimens are cooled to $300^{\circ}C$ at the rate of $2.4^{\circ}C/s$. Then the above-listed operations of heating to the carburization temperature, carburization proper, heating to the stage of diffusion saturation, diffusion saturation proper and cooling are repeated seven times more. Now the container is opened, the powder mixture is turned over for reclaiming and the specimens are tested for determining the physicomechanical and physicochemical properties of the deposited silicon carbide coating.

Test results:

- carbide coating is compact, i.e. practically without

pores;

- thickness of carbide coating, 39.8 μm ;
- microhardness of carbide coating, 22.3 GPa;
- average height of carbide crystals, 4.3 μm ;
- 5 - hardness of base material, 7.4 GPa;
- minimum hardness in sublayer zone, 7.4 GPa;
- relative wear rate, 20.9 $\text{g/m}^2 \text{ s}$.

Example 4

The diffusion carbide coatings are deposited in the
10 container described in Example 1. The container is charged
with 300 g of a powder mixture containing 195 g of chro-
mium powder (65%), 3 g of polyvinyl chloride (1%), 1.5 g of
ammonium fluoride NH_4F (0.5%) and 100.5 g of magnesium
oxide MgO (33.5%). The powder mixture is prepared as in
15 Example 1. The specimens are used and arranged in the con-
tainer also as in Example 1. The container with the powder
mixture and specimens is placed into a resistor furnace and
heated to 600°C. At this temperature the specimens are
carburized for 1.1 h and the carburized specimens are
20 heated to 1000°C at the rate of 2.1°C/s. At this tempera-
ture the surface of the specimens is diffusion-saturated
with chromium. The diffusion saturation is conducted in
the course of 1.7 h. On completion of diffusion saturation
with chromium the specimens are cooled to 450° at the rate
25 of 2.1°C/s. Then the above-listed operations of heating
to the carburization temperature, carburization proper,
heating to the stage of diffusion saturation, diffusion

saturation proper and cooling are repeated four times more. Then the container is opened, the saturating powder mixture is turned over for reclaiming and the specimens are tested to determine the physicomachanical and physicochemical properties of the deposited chromium carbide coating.

Test results:

- carbide coating is compact, i.e. practically without pores;
- thickness of carbide coating, $23.7 \mu\text{m}$;
- microhardness of carbide coating, 22.0 GPa;
- average height of carbide crystals, $5.4 \mu\text{m}$;
- hardness of base material, 5.6 GPa;
- minimum hardness of sublayer zone, 5.6 GPa;
- relative wear rate, $16.5 \text{ g/m}^2 \cdot \text{s}$.

Example 5

This example is an illustration of using the reclaimed powder mixture of the composition according to Example 1 and utilized according to Example 1.

Upon completion of the process the powder mixture is reclaimed. For this purpose it is ground in a jaw crusher and sifted through a vibrosieve with the mesh size not over $50 \mu\text{m}$ for obtaining a powder fraction with a particle size not under $50 \mu\text{m}$. The mixture is sifted and dried for 4 h at 140°C . Then to 266.5 g (88.8%) of this mixture the following components are added: 3.3 (1.1%) of diphenyl $\text{C}_{12}\text{H}_{10}$ previously dried at 60°C in the course of 0.5 h, 1.65 g (10%) of ammonium chloride first dried in the course

of 4 h at 140°C , 19.5 g (6,5 %) of dry chromium powder and 9.05 g (3%) of dried aluminium oxide. Now all the components are carefully mixed and the prepared powder mixture is loaded into a container described in Example 1.

5 The specimens described in Example 1 are placed into the container with the powder mixture and the container is placed into a resistor furnace. The container is heated to 630°C and the specimens are carburized at this temperature for 0.9 h. The surface of the specimens is saturat-

10 ed with carbon. Then the carburized specimens are heated to 1020°C at the rate of 1.5°C/s . This temperature is the one at which the surface of the specimens is subjected to diffusion saturation with chromium. The process of diffusion saturation with chromium is conducted in the course

15 of 1.4 h. Then the specimens are cooled down to 350°C at the rate of 2.2°C/s . Finally the above-listed operations of heating to carburization temperature, carburization, heating to the stage of diffusion saturation, diffusion saturation proper and cooling are repeated once more. The

20 container is then opened, the saturating powder mixture is turned over for reclaiming and the specimens are tested for the physicomechanical and physicochemical properties of the deposited chromium-carbide coating.

Test results:

- 25
- carbide coating is compact, i.e. practically without pores;
 - thickness of carbide coating, 22.5 μm ;
 - average height of carbide crystals, 5.1 μm ;

- hardness of base material, 4.2 GPa;
- minimum hardness in sublayer zone, 4.2 GPa;
- relative wear rate, $14.1 \text{ g/m}^2 \cdot \text{s}$.

Example 6

5 This example illustrates the deposition of a diffusion carbide coating according to the previously known method.

 The powder mixture is prepared, loaded into the container and the specimens are arranged therein as in Example 1.

10 The loaded container is placed into a resistor furnace and heated to 800°C . At this temperature the specimens are carburized for 3.5 h and their surface becomes carburized. Upon completion of the carburization period the specimens are heated to a temperature of diffusion saturation, i.e. to 1050°C . At this temperature the sur-
15 faces are diffusion-saturated in the course of 3.5 h.

 Then the container is withdrawn from the furnace and cooled naturally to room temperature. After cooling, the container is opened, the powder mixture is sent for reclaim-
20 ing and the specimens are tested for determining the physicochemical and physicochemical properties of the deposited chromium carbide coating.

Test results:

- carbide coating is compact, i.e. practically has
25 no pores;
- thickness of carbide coating, $12.3 \mu\text{m}$;
- microhardness of carbide coating, 21.3 GPa;

- average height of base material, $7.1\text{ }\mu\text{m}$;
 - hardness of base material, 6.4 GPa;
 - minimum hardness in sublayer (decarburized) zone, 5.8 GPa;
- 5 - depth of decarburized zone, $17\text{ }\mu\text{m}$;
- relative wear rate, $36.4\text{ g/m}^2\cdot\text{s}$.

 If we compare the physicommechanical and physicochemical properties of the specimens with a diffusion carbide coating deposited by the herein-proposed and previously
10 known methods, it can be concluded that the physicommechanical properties of the coating obtained according to the present invention are considerably higher than those of the coating deposited in accordance with the method known heretofore.

15 Thus, the wear resistance of the diffusion carbide coating produced in accordance with the disclosed invention under the conditions of abrasive wear is 2.8 - 3.3. times higher than the wear resistance of the diffusion carbide coating produced by the known method. Besides, the articles
20 with diffusion carbide coating deposited by the disclosed method have no decarburized zone under the coating.

Claims:

1. A method of depositing a diffusion carbide coating on an iron-carbon alloy article comprising the following sequential steps:

5 (a) loading a container with a powder mixture containing, as solid components, at least one carbide-forming element, at least one carbon-containing compound, an activator, and an inert filler, and immersing the article in the mixture;

10 (b) heating the immersed article to a temperature of carburization of its surface, in the range from 560 to 720°C;

15 (c) carburizing the surface of the immersed article at a temperature in the range from 560 to 720°C for a time period of from 0.6 to 1.2 h;

 (d) heating the carburized article at a rate of 0.8 to 2.4 °C/s to a temperature of diffusion saturation of its surface with the carbide-forming element(s), the said temperature being in the range from 950 to 1100°C;

20 (e) diffusion saturating the surface of the article with the carbide forming element(s) at a temperature in the range from 950 to 1100°C for a time period of from 1.2 to 1.8 h;

25 (f) cooling the article with the thus-deposited carbide coating at a rate of 1.2 to 2.4 °C/s to a temperature in the range from 300 to 500°C; and

(g) repeating the said steps (b) to (f) at least once.

2. A method as claimed in claim 1, in which the said steps (b) to (f) are repeated up to 7 times.

5 3. A method as claimed in claim 1 or 2, in which the powder mixture comprises 40 to 70 mass % of the carbide forming element(s), 0.5 to 2.5 mass % of the carbon-containing compound(s), 0.2 to 5.0 mass % of the activator, and the inert filler as the balance.

10 4. A method as claimed in any preceding claim, in which the or each carbon-containing compound is a hydrocarbon having a boiling or sublimation point of 100 to 700°C and being in a solid state at room temperature.

15 5. A method as claimed in any preceding claim, in which the or each carbon-containing compound is selected from diphenyl, naphthalene, anthracene, pyrene, triphenylene, and 3,4-benzo-pyrene.

6. A method as claimed in any preceding claim, in which the activator is at least one ammonium halide.

20 7. A method as claimed in any preceding claim, in which the inert filler comprises at least one of aluminium oxide, magnesium oxide, and silicon dioxide.

8. A method as claimed in any preceding claim, in which the particle size of the powder mixture does not exceed 50 μm .

9. A method of depositing diffusion carbide coatings on iron-carbon alloy articles, substantially as described in any of Examples 1 to 5.